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(56) Documents Cited

GB 2309703 A	GB 2266179 A	EP 0803925 A
DE 004015147 A	US 5693433 A	US 5658586 A
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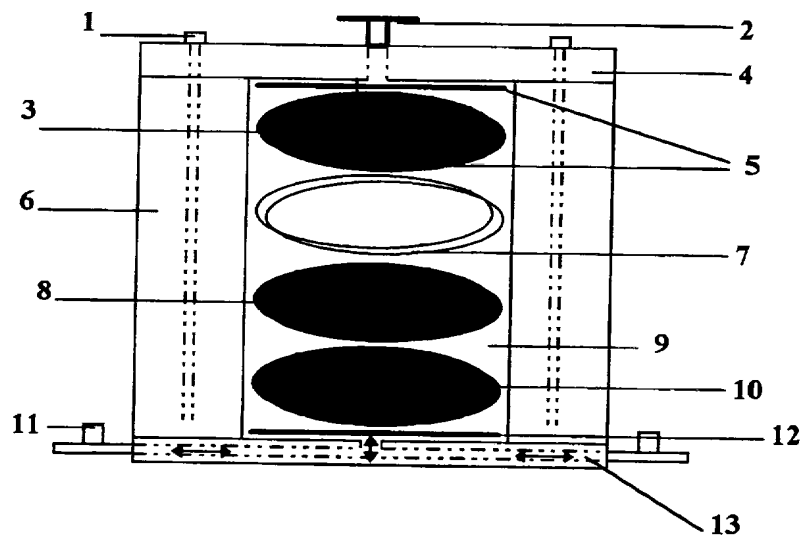
Non-aqueous electrochemical cell containing conjugated polyimine functionality coupled to sulphur trioxide

(57) A novel rechargeable lithium battery is disclosed wherein the positive electrode is comprised of conductive polymeric materials having conjugated imine functionality and the lithium salt of a sulphur oxy-acid as the active redox component. On charging, lithium metal is electrochemically split from the salt, e.g. Li_2SO_3 , and is deposited at the negative electrode, the imine sites at the positive electrode acting as host for SO_3 complex formation. The system is optimized when the nitrogen content of the polyimine host material is present in an equimolar ratio with SO_3 .

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Figure 1:



Key:

- 1 retaining bolt (1 of 6)
- 2 valve
- 3 piston & contact
- 4 cell top
- 5 O-rings
- 6 cell body
- 7 separator
- 8 polymer adduct
- 9 cell bore
- 10 gauze
- 11 valve
- 12 O-ring
- 13 base plate

**Non-Aqueous Electrochemical Cell
Containing Conjugated Polyimine
Functionality Coupled To Sulphur Trioxide**

Background To The Invention:

An outstanding need exists for more efficient storage of electrical energy by redox chemical conversion. At present, most applications for a rechargeable or secondary battery system are met by either the lead-acid or the nickel-cadmium types, these being capable of storing a maximum of around 35 WhKg^{-1} of battery weight. For electric vehicles to be viable, the energy density available from existing systems is totally inadequate and this restricts the development of vehicles to compete with those powered by internal combustion engines. In the field of portable communications equipment, the need for greater amounts of electrical energy to be stored in handsets is a top priority.

A target energy density of 100 WhKg^{-1} is generally regarded as being an acceptable and realistic value for the new generation of rechargeable batteries. In order to realize this threefold increase over existing electrochemical systems, it is necessary to resort to non-aqueous media. Primary, or non-rechargeable, battery systems based on lithium metal as the negative electrode are capable of delivering over $1,000 \text{ WhKg}^{-1}$ are now well established. The lithium thionyl chloride system is a good example of a high energy couple but is not rechargeable. Sodium / sulphur and sodium / metal chloride systems under development are reported to have good reversibility and to give energy densities in excess of 100 WhKg^{-1} . These systems have an operating temperature of *ca.* 350°C which limits their viability and increases safety concerns.

It is an important objective of the present invention that the chosen electrochemical system is operational at ambient temperatures. This obviates the need for the use of an external heating source. This is achieved by the use of electrolytes based on non-aqueous solvents which remain in the liquid phase over a broad temperature window and also have good ionic conductivity. Suitable electrolytes consist of organic or inorganic solvents or mixtures thereof, with salts of the alkali or alkaline earth metal which forms the negative electrode dissolved therein.

A non-rechargeable lithium battery system, well known as a power source for heart pacemakers, comprises a positive electrode which is a complex compound of iodine and poly(2-vinyl pyridine), P(2-VP)-I_2 . In this system, the P(2-VP) polymer material forms a solid solution with iodine and regulates reaction of the latter with lithium metal since there is no discrete separator present. This system is not reversible and has a very low rate capability.

By contrast, a very high rate primary lithium system uses liquid sulphur dioxide, SO_2 , as active positive electrode material, the SO_2 also serves as electrolyte solvent or co-solvent. This system can be discharged at high rates down to -40°C , but extensive development work aimed at making it rechargeable has met with only limited success. It is a major objective of the present invention to provide a polymeric material comprised of imine functionality which forms an insoluble complex with a highly active Lewis acid such as SO_2 or SO_3 and confer much higher rate capability than that achieved in the P(2-VP)-I_2 system but be electrochemically reversible.

It has been known for some time that a solution of sulphur trioxide containing an ionically conducting lithium salt exhibits an EMF of *ca.* 4.5 V. Attempts to utilise such an electrochemical cell have been unsuccessful primarily due to the high reactivity of SO₃ to other cell constituents including separator, cell wall and lithium electrode itself. Solid complexes are formed by combination of SO₃ with monomeric tertiary amines and imines, including heterocyclic compounds such as pyridine and these are stable in the absence of moisture to *ca.* 200°C. These complexes are unsuitable as positive electrode materials because of their ready solubility in excess SO₂, SO₃ and other highly polar solvents.

In UK Patent Application GB 2 266 179 A, electrochemical cells were claimed having complexes of SO₃ and polymeric tertiary amines. The energy densities of these are low due to the high ratios of carbon to nitrogen functionality.

Invention:

This present invention is concerned with a novel positive electrode composition for electrochemical cells of the non-aqueous type. A high energy and power density together with superior charge retention over prior art systems are salient features of the new electrode composite as is the relatively low cost and non-toxicity of the starting materials. The invention offers an improved power storage device viz. an electric battery or capacitor and is based on the use of an organic polymer having a C to N ratio of no more than 3 to 1 and in which conjugated imine functionality is present in a 1 : 1 molar ratio of N : SO₃. The positive electrode may be prepared by the thermal cyclization of nitrile containing polymers such as acrylonitrile or copolymers thereof such as fumaronitrile, or maleonitrile. When thermally restructured at temperatures of up to 600°C in an anaerobic environment, conjugated arrays of imine functionality are incorporated into the material.

In one example of the invention, the organic polymer is finely ground with Li₂SO₃ to form an intimate admixture in which there is a 1 : 1 molar ratio of N : SO₃. This combination of polymer host and discharged product is pressed into a tablet and assembled in an arrangement where it is positioned between an aluminium plate positive electrode current collector and copper negative electrode; a conventional separator is also employed in the assembly. A non-aqueous electrolyte and background salt, such as LiPF₆, is employed to provide an ionic conduction pathway.

Charging causes lithium to be electroplated at the negative electrode while SO₃ is able to form stable complexes with imine functionality in the organic polymer. Discharging causes the recombination of lithium with SO₃ complexes. In this invention, SO₃ acts not only as polymer "dopant" but also as sites for the reversible redox electrochemistry of Li₂SO₃.

The cell performance is improved when PVDF, present by weight as 5%, is employed as binder with the polymer admixture. Carbon black, up to 20% by weight, is also employed to provide greater electronic conduction.

The present invention provides an electrochemical cell in which SO₃ is immobilised on a polymeric network comprised of a conjugated arrays of imine functionality. These tertiary nitrogen sites act as hosts to SO₃ complex formation. The requisite source materials are derived from the polymerization of monomers in which either (a) tertiary nitrogen is present in the form of an unsaturated side chain, as is the case in acrylonitrile, cyanoacetylene, dicyanoacetylene, *etc.*, or (b) unsaturated tertiary nitrogen is present in the monomer backbone and it acts as sites for chain or addition growth polymerization, as is the case in fumaronitrile, malononitrile, maleonitrile, *etc.*, or (c) unsaturated tertiary nitrogen is formed from the oxidative dehydration / polymerization of monomers in which non-tertiary nitrogen is present, as is the case in oxamide *etc.*, or (d) the thermal cyclization / polymerization of nitrile functionality contained within (a) - (c). A solid insoluble complex is formed by direct combination of SO₃ with such polymers.

Many polymeric structures fall within the scope of this invention. The examples below are selected because they are either readily available or are synthesized either as homopolymer or as copolymers with other monomers within this list of materials:

- poly(2-vinyl pyridine)
- poly(4-vinyl pyridine)
- poly(acrylonitrile) thermally restructured
- poly(N-vinyl pyrrole)
- poly(N-methyl pyrrole)
- poly(fumaronitrile) thermally restructured
- poly(cyanoacetylene) thermally restructured
- poly(dicyanoacetylene) thermally restructured

The composite positive electrode is formed by the combination of SO_3 with the polymer at imine (tertiary nitrogen) sites in an equimolar ratio, *i.e.* a 1 : 1 equivalence of N : SO_3 functionality. In this invention, the specific discharge capacity of electrochemical cells is optimized when positive electrode complexes are comprised of this ratio of imine host : SO_3 , although other ratios approaching parity also yield cells with significantly high values for energy density. For the intended application, it is essential that the polymer and SO_3 , used in preparation of the composite electrode, are completely anhydrous.

In accordance with the invention, there is provided an electrochemical cell, the positive electrode of which is comprised of an imine-containing polymer / SO_3 complex as previously described in contact with a suitable current collector. Certain polymers of the conjugated type, an example of which is poly(N-methyl pyrrole) or thermally cyclized poly(acrylonitrile), are sufficiently electronically conductive to carry current from the reactive sites in the complex to the positive terminal. Non-conductive polymers require the use of carbon black or similar finely divided inert conductive material to be in intimate contact with the polymer complex. The negative electrode of the cell may be a light metal or light metal alloy. Lithium is the preferred negative electrode, yielding the greatest energy density and voltage. Alloys of lithium with aluminium or a carbon intercalate may be used to improve the electrochemical stability to the electrolyte. For high rate applications, anhydrous liquid electrolytes are required by virtue of their high ionic conductivity. Solid polymer electrolytes may also be used for low rate applications. Lithium ion conductivity is achieved in both instances by the incorporation of suitable salts such as LiCF_3SO_3 and / or LiPF_6 . Liquid electrolytes may consist of mixtures of aprotic organic solvents and / or liquid SO_2 . Preferred materials are fluoropolymers such as Tefzel™ (Dupont) or poly(vinylidene fluoride) which resist attack from the strongly oxidizing SO_3 / polymer positive electrode complex.

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Example:

Fresh, thermally restructured poly(acrylonitrile), or alternatively poly(acrylonitrile-fumaronitrile) copolymer (of various comonomer mole % ratios), powder (*ca.* 5g.) was transferred into a glove box maintained under a steady flow of dry nitrogen (white spot, BOC). Thermally restructured poly(acrylonitrile) (0.700g. acrylonitrile) was weighed into a quartz mortar and pestle. Lithium sulphite (1.242g.) was then added followed by graphite (0.225g. 9.2 % w/w, Timcal SFG-44) carbon (0.225g. 9.2 % w/w, Sedema MMM Super P) and PVDF binder (0.053g. 2.2 % w/w, Elf-Atochem Kynar 741). The five components were thoroughly ground together by use of the pestle to produce a very fine, homogeneous, charcoal coloured material. This was then heated on a hot plate (*ca.* 80 - 100°C) for *ca.* 30 minutes under an anaerobic environment of dry $N_2(g)$.

After application of 30 minutes of heating, the adduct (0.2g.) was pressed in to a small disc of diameter 25 mm and *ca.* 0.5 mm thick by the use of a Specac press operated at 15 tonnes. The electrochemical test cell (Figure 1) was then inverted so that copper piston (negative electrode) faced uppermost. A poly(propylene) separator (Celgard 3501, Hoecht Celanese) of diameter 27mm was cut out and placed on the surface of the copper piston. The stainless steel piston from the Specac press was used to press down gently on to the Celgard so that the excess of separator was creased to form a shallow cup. Dry (17 ± 3 ppm H_2O) electrolyte (1 mol.dm^{-3} $LiPF_6$ in equal weights of ethylene carbonate and diethyl carbonate, Merck) was carefully added drop-wise onto the surface of the separator by the use of a pipette so that it was barely moistened. The disc of adduct was then placed onto the separator and a further addition of electrolyte was pipetted on the surface. A piece of expanded aluminium gauze was then placed on top of the adduct. This acted as an electrical contact to the aluminium base and it also provided torsional rigidity to the adduct. The remains of the test cell were then assembled and the six securing bolts (see Figure 1) were torqued evenly.

The active material of each adduct was formulated employing a 1 : 1 ratio of N : SO_3 for each thermally restructured polymer tested. Owing to the low intrinsic electronic conductivity of both Li_2SO_3 and the thermally treated polymers, an additional mass of graphite and carbon (up to 10 % by weight each) was introduced to all adducts. The brittle nature of the resultant materials meant that a binder was required to consolidate the electrodes into a suitable form. Finely divided poly(vinylidene fluoride), PVDF, was employed to facilitate this need. After thorough mixing and grinding of thermally treated polymer, lithium sulphite, graphite, carbon and binder, admixtures were pressed into discs of diameter 2.5cm (area 4.91 cm^2) to fit the internal bore of both cell types. Figure 1 is a pictorial representation of the cell assembly.

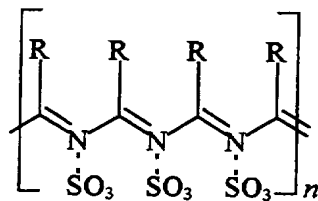
All electrochemical cycling was performed at a constant current of 1mA (*i.e.* 0.20 mA.cm^{-2}). A Lee Dickens potentiostat regulated charge cycles between 2.4 and 4.3 V employing an internal shunt which applied a variable impedance of 1000 mVmA^{-1} for discharge cycles and 10 mV / mA

for charge cycles. During discharge, current drain was maintained at 1mA and the voltage was permitted to operate in the 2.4 - 4.3 V window. Discharges were halted automatically by an internally programmed trip which was effected if the voltage dropped below 2.4 V. All charge and discharge cycles were conducted for 5 hours apiece such that a maximum of 5 mAh of charge was administered or drained during any individual cycle. For each cell tested, the current density and operating voltage window was maintained at 0.20 mAcm^{-2} and 2.4 - 4.3 V respectively such that the only significant varying parameter between experiments was the composition of the positive electrode complex.

Data was initially presented in the form of chart overlays of voltage versus time (units of 1cm also represented the flow of 1 mAh of charge). Accurate validation of charge flow was performed by the integration of numerical data performed by the Lee Dickens potentiostat. Thus, direct comparisons of charge and energy flow were possible for each thermally treated polymer. The mass of each adduct was measured so that values for specific energy were also expressed for each system. A control experiment was performed using an adduct of graphite, carbon and lithium sulphite (1 : 1 molar equivalent of SO_3 : graphite and 20% carbon weight). This was intended to demonstrate the effect of no imine presence in the adduct and test the validity of SO_3 / imine complex.

Claims:

1. An electrochemical cell characterized in that the positive electrode consists of a macromolecular complex of SO_3 and a polymeric substance comprised of arrays of imine functionality containing tertiary nitrogen as the recurring structural unit represented by the formula:



where R is an alkyl or alkylene group or R groups may be inter-linked to be representative of a closed 5 or 6 membered cyclic structures akin to the ring systems of pyrrole or pyridine, respectively. Additionally, R groups are inter-linked and form the mirror image of conjugated imine functionality already represented, *i.e.* the polymer as a whole is comprised of double ladders of imine moieties, as is representative of poly(pyrazino-pyrazine). The said positive electrode being used in conjunction with a non-aqueous electrolyte and a negative electrode consisting of a light metal or light metal alloy.

2. An electrochemical cell according to claim 1, in which the polymeric substance is thermally restructured poly(acrylonitrile).
3. An electrochemical cell according to claim 1, in which the polymeric substance is thermally restructured poly(acrylonitrile-fumaronitrile) copolymer.
4. An electrochemical cell according to claim 1, in which the polymeric substance is thermally restructured poly(acrylonitrile-2-vinyl pyridine) copolymer.
5. An electrochemical cell according to claim 1, in which the polymeric substance is thermally restructured poly(acrylonitrile-4-vinyl pyridine) copolymer.
6. An electrochemical cell according to claim 1, in which the polymeric substance is poly(pyrazino-pyrazine).
7. An electrochemical cell according to claim 1, in which the polymeric substance is poly(cyanoacetylene).
8. An electrochemical cell according to claim 1, in which the polymeric substance is poly(dicyanoacetylene).
9. An electrochemical cell according to claim 1,2,3,4,5,6,7 and 8 in which the preferred ratio of SO_3 to nitrogen in the SO_3 / polymer complex is 1 : 1.
10. An electrochemical cell according to claim 1, in which the polymer has a conjugated array of double bonds which confers intrinsic conductivity to the material and obviates the need to include carbon or other materials in the positive electrode which enhance electronic conductivity.

11. An electrochemical cell according to claims 1 to 10, in which the negative electrode is lithium metal and the electrolyte is a solution of a lithium salt in aprotic solvents.
12. An electrochemical cell according to claims 1 to 10, in which the negative electrode is magnesium metal and the electrolyte is a solution of a magnesium salt in aprotic solvents.
13. An electrochemical cell according to claims 1 to 11, in which the electrolyte consists essentially of a solution of lithium salts in liquid SO_2 .
14. An electrochemical cell according to claims 1 to 9, in which the electrolyte consists of a solid polymer composition made ionically conductive by the incorporation of appropriate lithium salts.
15. An electrochemical cell according to claims 1 to 14, which forms the unit for a rechargeable battery.
16. An electrochemical cell according to claims 1 to 14, which forms the unit for a super or ultra-capacitor.
17. This invention is demonstrated to work according to claims 1 to 15, and be optimized in which the positive electrode is comprised of a polymeric material in which the ratio of carbon to imine functionality is present between the values 1 : 1 and 3 : 1, some examples of which are included in claims 2 to 6.



Application No: GB 9804958.8
Claims searched: All claims

Examiner: A.R.Martin
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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): H1B

Int Cl (Ed.6): H01M 10/00

Other: On line databases WPI, EDOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP0803925 A	Japan Storage see column 10 lines 12-26	Claim 1 at least
X	GB2309703 A	AEA see claim 6	"
X	GB2266179 A	Gilmour see claim 3	"
X	US5693433 A	Technology Resources see claim 1	"
X	US5658686 A	Sony see claim 4	"
X	US4879192 A	Hitachi see column 2 lines 2-40	"
X	DE 4015147 A	Komb Veb see abstract	"

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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ABSTRACT:

CHG DATE=20040619 STATUS=N>A novel rechargeable lithium battery is disclosed wherein the positive electrode is comprised of conductive polymeric materials having conjugated imine functionality and the lithium salt of a sulphur oxy-acid as the active redox component. On charging, lithium metal is electrochemically split from the salt, e.g. Li_2SO_3 , and is deposited at the negative electrode, the imine sites at the positive electrode acting as host for SO_3 Complex formation. The system is optimized when the nitrogen content of the polyimine host material is present in an equimolar ratio with SO_3 .